

M1. *Ab Initio* Study on the Oxidation of NCN by O and HO Radicals: Prediction of the Total Rate Constant and Product Branching Ratios

R. S. Zhu^a and M. C. Lin^b

^a Department of Chemistry, Emory University, 1515 Dickey Dr., Atlanta, GA 30322

E-mail: rzhu@emory.edu

^b Department of Chemistry, Emory University, 1515 Dickey Dr., Atlanta, GA 30322

E-mail: chemmcl@emory.edu

NCN is the major product formed in the CH + N₂ reaction. In view of the absence of NCN kinetic data in the literature, particularly for its oxidation by O and OH which are crucial to our understanding of the prompt NO formation chemistry, the mechanisms and rate constants of these oxidation reactions are examined in this work. The potential energy surfaces (PES) shown in Figs. 1 and 2 have been calculated with the highest scheme of the modified Gaussian-2 method G2M(CC1) [1]. The rate constants and branching ratios for the low-lying channels for both systems were calculated by Variflex [2] and ChemRate [3] programs.

For the NCN + O reaction, the rate constants of the dominant channels were calculated in the temperature range of 200 – 3000 K:



which can be expressed as: $k_1 = 8.40 \times 10^{-12} T^{0.17} \exp(17/T)$, $k_2 = 3.34 \times 10^{-11} T^{0.15} \exp(16/T)$ and $k_{(1+2)} = 4.15 \times 10^{-11} T^{0.16} \exp(17/T)$ in the units of cm³ molecule⁻¹ s⁻¹. The rate constant for the formation of CO + N₂ was also calculated, which is 3 - 5 orders of magnitude lower than that of the formation of CN + NO. It can be expressed as: $k_{(\text{CO} + \text{N}_2)} = 1.87 \times 10^{-23} T^{2.63} \exp(587/T)$ cm³ molecule⁻¹ s⁻¹.

For the NCN + OH reaction, the rate constants of the association and the formation of H + NCNO and HCN + NO can be expressed as: $k_{\text{ass}} = 5.1 \times 10^{-97} T^{-31.8} \exp(-32194/T)$, $k_{\text{NCNO}} = 2.56 \times 10^{-18} T^{-1.90} \exp(-2242/T)$, $k_{\text{HCN}} = 3.71 \times 10^{-13} T^{0.35} \exp(-2346/T)$ with the units of cm³ molecule⁻¹ s⁻¹, respectively, in the temperature range of 1000-2500 K.

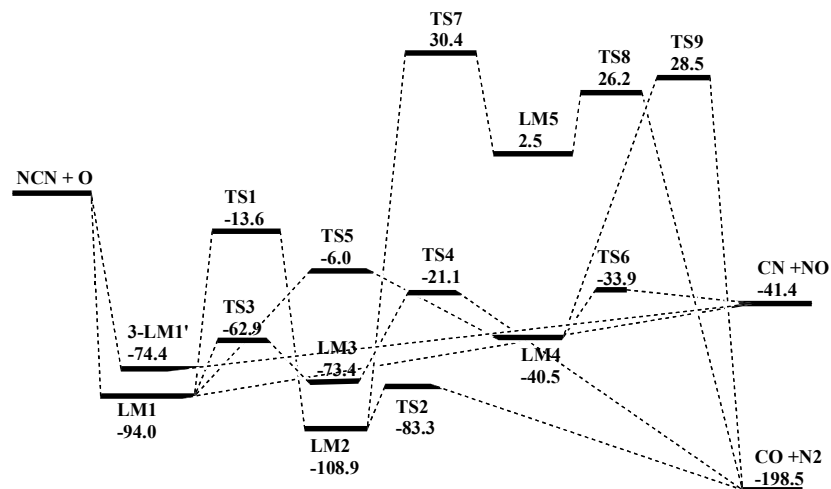


Figure 1. PES diagram of $\text{NCN} + \text{O}$ reaction calculated at the G2M(CC1) level.

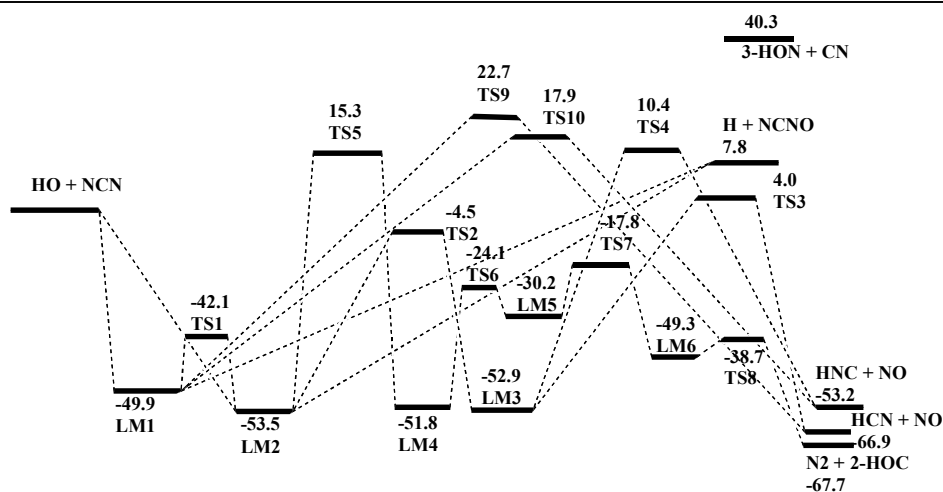


Figure 2. PES diagram of $\text{NCN} + \text{OH}$ reaction calculated at the G2M(CC1) level.

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M2. Theoretical Analysis of the Thermal Three-Channel Decomposition of Formaldehyde

Juergen Troe

Institute of Physical Chemistry, University of Goettingen, Tammannstrasse 6, D-37077, Goettingen, Germany, email: shoff@gwdg.de

The thermal unimolecular dissociation of formaldehyde proceeds on three channels, the molecular elimination channel $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$, the radical-forming bond fission channel $\text{H}_2\text{CO} \rightarrow \text{H} + \text{HCO}$ and a third bond-fission initiated channel $\text{H}_2\text{CO} \rightarrow \text{H} \cdots \text{HCO} \rightarrow \text{H}_2 + \text{CO}$ which also forms molecular products [1,2]. This talk provides a quantitative analysis of the reaction. It shows that the kinetics is governed by a subtle superposition of collisional channel-coupling to be treated by solving a master equation [3], of rotational channel-switching [4] accessible through ab initio calculations of the potential and spectroscopic determinations of threshold energies, and channel-branching above the threshold energy for radical formation which can be quantified by classical trajectory calculations [2] and photolysis quantum yields [5,6]. By fitting a single unknown parameter, the average total energy transferred per collision, from the measured low pressure rate coefficient for formation of molecular fragments at 2000 K, low pressure rate coefficients for formation of radicals and molecular products at other temperatures are modelled and found to be in good agreement with the available experiments, see [7-9] and earlier references cited therein. The modelled rate coefficients [10] over the range 1400 – 3200 K in the bath gas Ar are represented by

$$k_{0,\text{Mol}}/[\text{Ar}] = 4.1 \times 10^{-7} (\text{T}/2000 \text{ K})^{-2.6} \exp(41210 \text{ K}/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_{0,\text{Rad}}/[\text{Ar}] = 1.8 \times 10^{-7} (\text{T}/2000 \text{ K})^{-2.1} \exp(-43640 \text{ K}/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

for molecular and radical products, respectively. The formaldehyde system particularly well demonstrates that multiple couplings between the channels have to be accounted for in multichannel unimolecular dissociation reactions. A separate treatment of decoupled individual channels misses important aspects of the dynamics.

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M3. *Invited:* Toward a Systematic Validation of Quantum Chemistry in Computational Kinetics

C.A. Gonzalez

Computational Chemistry Group, Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, MD. 20899

The use of modern computational chemistry methodologies in the prediction of molecular properties has become increasingly popular mainly due to significant improvements in the algorithms, the accuracy of the methods, and the advent of powerful computer resources. This is particularly true in the area of thermochemistry, where researchers in industry and academia perform quantum chemistry calculations on a routine basis. Despite this progress, the use of similar methodologies in computational kinetics has been slow. In fact, computational kinetics remains an obscure area being used most of the time by experts in the field. There is no doubt that the application of quantum chemistry calculations in the area of computational kinetics will have a significant impact. In order for this to happen, however, it is critical that reliable state-of-the-art methodologies be widely available to the scientific community. In order to achieve this goal, an exhaustive and systematic validation of these methodologies is necessary. However, in stark contrast to the case of thermochemistry, determining error bounds in the properties computed by quantum chemistry methods necessary for the prediction of rate constants have been found to be a daunting task. In this talk, the difficulties related to the validation process of quantum chemistry methods in computational kinetics will be discussed. In addition, possible strategies that could potentially lead to a systematic approach in the validation of these methodologies will also be presented.

M4. Decomposition Pathways of Vinyoxy and Acetyl Radicals

Juan P. Senosiain^a, Stephen J. Klippenstein^b, James A. Miller^c

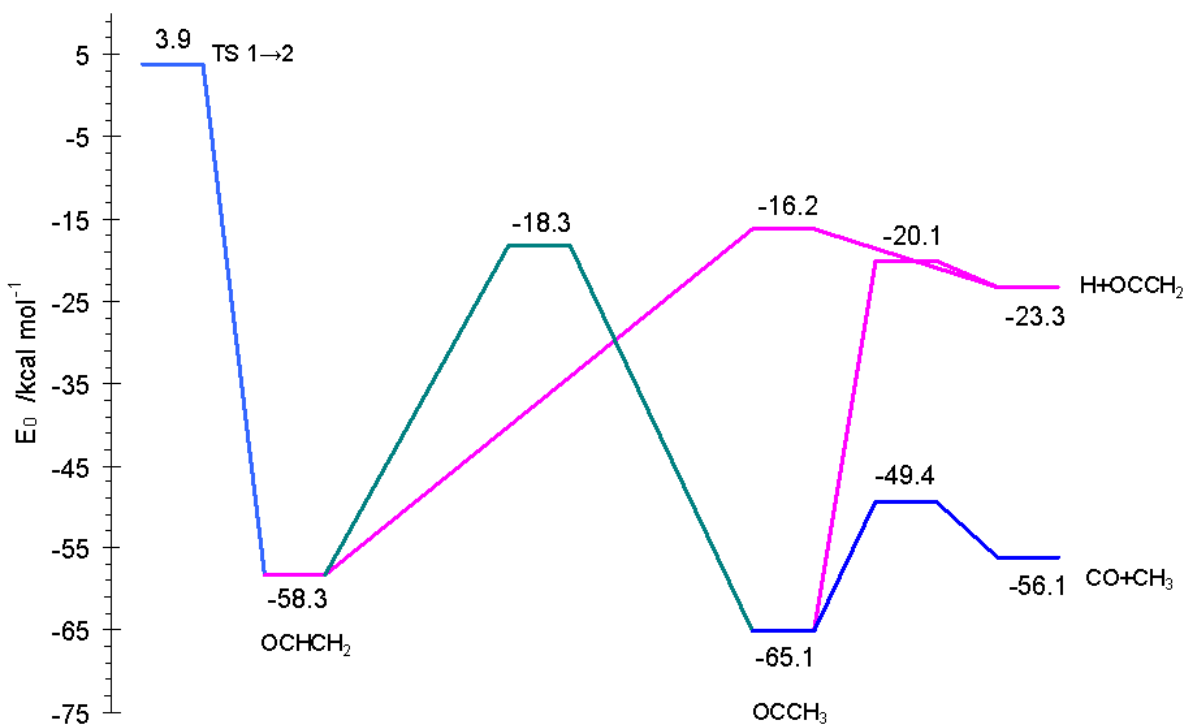
Combustion Research Facility, Sandia National Laboratories,
Livermore, California 94551-0969 MS 9055

^a E-mail: jpsenos@sandia.gov

^b E-mail: sjklipp@sandia.gov

^c E-mail: jamille@sandia.gov

The potential energy surface for the decomposition of ground-state vinyoxy and acetyl radicals has been calculated using the RQCISD(T) method and extrapolated to the infinite basis set limit. Rate coefficients for the decomposition pathways of these two radicals were calculated using the master equation and variational transition state theory. Our calculated rate coefficients for the association of H+ketene are in excellent agreement with the experimental data after a minor adjustment to the energy barrier (< 1 kcal/mol).



Simplified $\text{C}_2\text{H}_3\text{O}$ PES for $\text{H}+\text{CH}_2\text{CO}$

Microcanonical rate coefficients for the decomposition of vinoxy radicals indicate a prevalence of the CH_3+CO channel at internal energies below 7100 cm^{-1} . At higher energies, the $\text{H} + \text{ketene}$ channel is dominant, in agreement with the results of Osborn et al[1] who predicted a ketene/methyl ratio of about 3.3 at photodissociation energies. Interestingly, the calculated thermal rate coefficients for vinoxy decomposition show mainly $\text{CO}+\text{CH}_3$ products below 2500 K. Acetyl radicals decompose almost exclusively to $\text{CO}+\text{CH}_3$. Agreement with experimental data between 300 and 500 K is very good.

Acknowledgements:

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M5. Spin-forbidden Association Reactions in Sulfur Chemistry: Comparison of $O + SO_2$ and $S + NH_3$ Addition with Spin-allowed $S + NO$ recombination

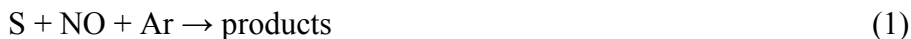
A. Goumri, J. Naidoo, Y. Gao, D.D. Shao and Paul Marshall^a

Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203-5070, USA

^aE-mail: marshall@unt.edu

Sulfur is known to influence NO_x formation in flames but the mechanism is unknown. There may be direct sulfur-nitrogen interaction, or sulfur may affect the overall radical pool. In this context the title reactions have been studied by the laser photolysis – resonance fluorescence technique, at temperatures up to 1000 K and pressures of Ar bath gas up to 800 mbar.

In the case of



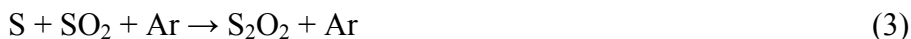
simple third order kinetics are observed (contrary to prior experiments, made at room temperature, which suggested fall-off behavior [1]). The third-order recombination rate constant drops with increasing temperature. RRKM modeling of this process rationalizes our experiments. ONS is the likely dominant product. Ab initio calculations reveal other slightly less stable isomers of ONS, and other reaction paths such as abstraction and addition of S to the oxygen end of NO are discussed.

Our extended T and p measurements on the spin-forbidden process



reveal for the first time (1) a predicted maximum in the recombination rate constant at about 800 K, and (2) fall-off behavior. The results can be rationalized in terms of Troe's approximate master equation formalism, and extrapolated to yield the high-pressure limit. The addition reaction occurs over a significant barrier. A simple model [2] of the intersection of the singlet and triplet curves gives information about the probability of intersystem crossing, which leads to a small pre-exponential factor at the high-pressure limit. Ab initio calculations indicate the existence of a new bound triplet state for SO₃.

Initial results for the analogous process



are discussed briefly in terms of the same model.

Similarly, our first measurements of



indicate the recombination rate constant is close to the high-pressure limit, which is small compared to typical values for spin-allowed addition reactions. Possible adducts are characterized by ab initio methods, and the results used to apply Troe's formalism.

This work was supported by the National Science Foundation (Grant CTS-0113606), the Robert A. Welch Foundation (Grant B-1174) and the UNT Faculty Research Fund.

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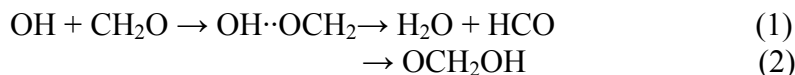
M6. *Ab Initio* Study of the OH + CH₂O Reaction: The Effect of the OH··OCH₂ Complex on the H-Abstraction Kinetics

Shucheng Xu, R. S. Zhu, and M. C. Lin

Department of Chemistry, Emory University, Atlanta, GA 30322.

Email (MC Lin): chemmcl@emory.edu.

The reaction of OH radical with formaldehyde (CH₂O) is one of the most critical reactions in the combustion of hydrocarbons, [C,H,O,N]-containing nitramine propellants and nitrate ester oxidizers. In this presentation, we report the result obtained by a high-level quantum chemical and statistical theory calculation, which correlates reasonably well with the experimental data. As shown in **Figure 1**, the geometries of all species involved have been optimized at the B3LYP/6-311+G(3df,2p) and CCSD/6-311++G(d,p) levels, respectively. Their relative energies improved by single-point calculations at the CCSD(T)/6-311+G(3df,2p) level based on the geometries optimized at the B3LYP/6-311+G(3df,2p) (CCSD(T)-1) and CCSD/6-311++G(d,p) (CCSD(T)-2) levels. The rate constants of reaction channel (1) producing H₂O + HCO and (2) giving the hydroxylmethoxy radical are calculated by the Variflex code based on the PES calculated using the CCSD(T)-1 and CCSD(T)-2 methods with the corresponding the optimized geometries and frequencies.



The existence of the molecular complex at the entrance channel has a significant effect on the predicted rate constant due to multiple reflections above the well of the complex, particularly for reaction (1). The predicted total rate constants ($k_1 + k_2$) with and without multiple reflections based on the PES calculated using the CCSD(T)-2 method and total rate constants with multiple reflections based the PES calculated using CCSD(T)-1 method are presented in **Figure 2** together with the experimental data. The predicted values with multiple reflections based on the PES calculated using the CCSD(T)-2 method are in good agreement with the experimental data for the whole temperature region within the scatters of the data. The predicted individual rate constants given in units of cm³ molecule⁻¹ s⁻¹ can be represented by

$$\begin{aligned}k_1 &= 2.45 \times 10^{-21} T^{2.98} \exp(1750/T) \quad (200 - 400 \text{ K}) \\ &= 3.22 \times 10^{-18} T^{2.11} \exp(849/T) \quad (400 - 3000 \text{ K}) \\ k_2 &= 1.05 \times 10^{-17} T^{1.63} \exp(-2156/T) \quad (200 - 3000 \text{ K}).\end{aligned}$$

The result indicates that k_2 accounts for 1% of the total rate constant at T = 1000 – 1600 K. The predicted total rate constants with multiple reflections based the PES calculated using CCSD(T)-1 method are lower 10-20% than the experimental data.

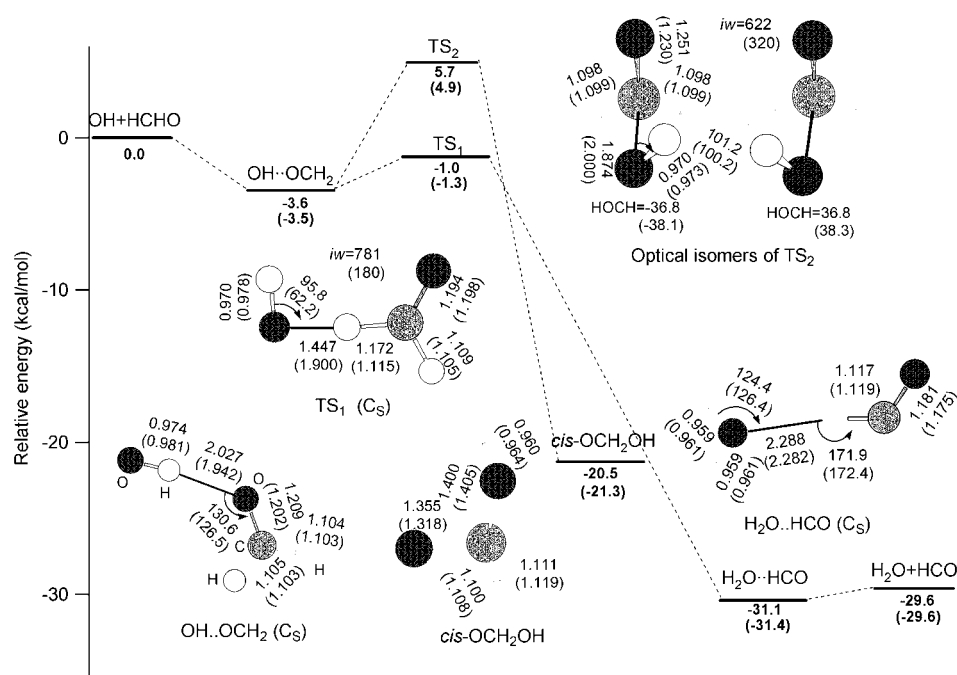


Figure 1. The PES for the reaction $\text{OH} + \text{CH}_2\text{O}$ computed at the CCSD(T)/6-311+G(3df,2p) level with the optimized geometries obtained at the CCSD/6-311++G(*d,p*) and B3LYP/6-311+G(3df,2p) (in parenthesis) levels.

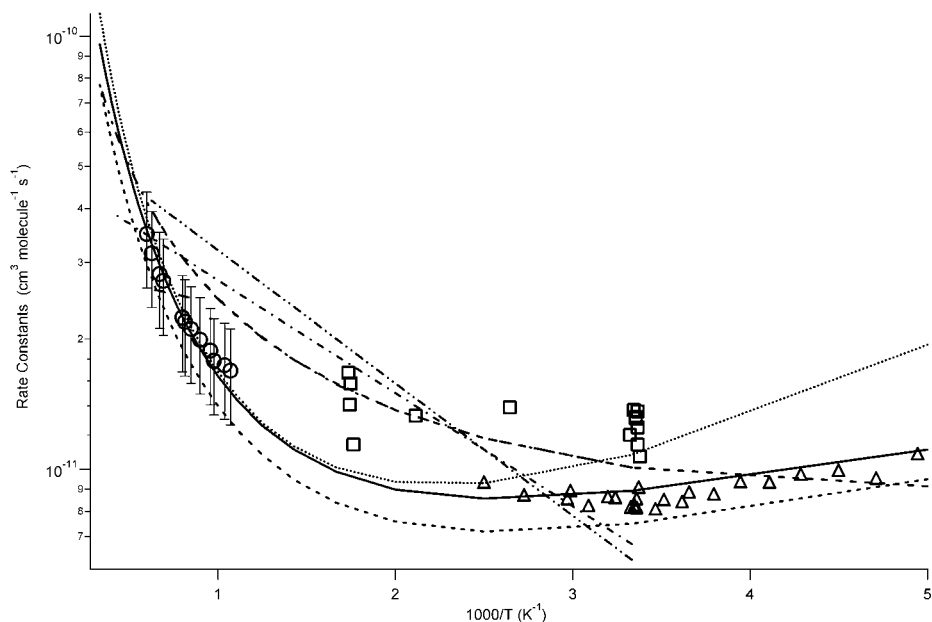


Figure 2. The predicted total rate constants with multiple reflections (solid curve) and without multiple reflections (dotted curve) based on CCSD(T)-2 method; total rate constants with multiple reflections based on CCSD(T)-1 method (dashed curve). The other lines and markers are the experimental data.

M7. Low Energy Mechanisms of Isotopic Exchange in The Gas Phase Reaction Between D₂O and H⁺(H₂O)_N (N=2-5)

Massimo Mella^a and Alessandro Ponti^b

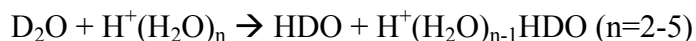
^aSchool of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT (UK)

E-mail: mellam@cf.ac.uk

^bConsiglio Nazionale delle Ricerche, Istituto di Scienze e Tecnologie Molecolari, via Golgi 19, 20133 Milano (I)

E-mail: alessandro.ponti@istm.cnr.it

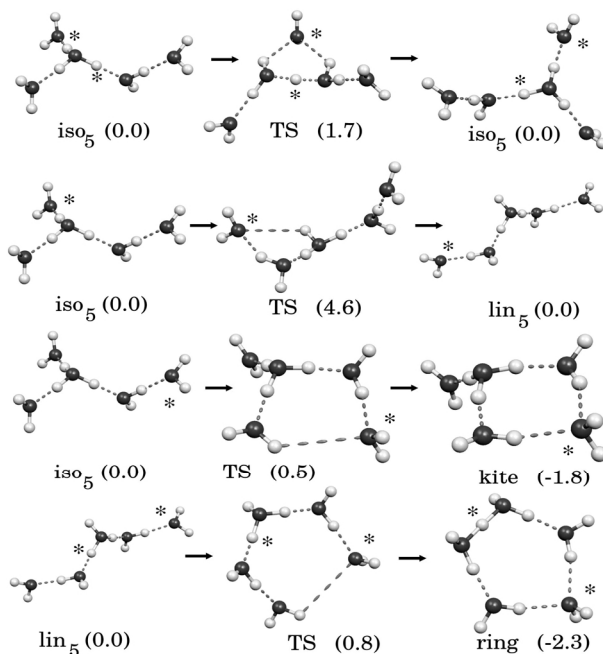
Molecular dynamics (MD) trajectories and high level *ab initio* methods have been used to study the low energy mechanism for the reaction



previously investigated experimentally in Refs. [1-4].

At low collisional energies, MD simulations show that the collisional complexes are long lived (estimated life-times > 10 ns) and undergo fast mono-molecular isomerization processes, converting their structure between different isomers within the 50-500 ps time scale.

Such processes, primarily involving water molecule shifts along a water chain, require surmounting very low energy barriers as computed using the CP-MP2/aug-cc-pVDZ level. As an example, the reactant, product and transition state of some of the isomerization processes identified during the MD simulation of the protonated pentamer are shown in the figure below together with their relative energetics (CP-MP2/aug-cc-pVDZ level).



For all the clusters, the conversion processes present sizable non-RRKM effects interpreted as a

lack of randomization of the internal kinetic energy. Also, the rate of water shifts was found to increase upon increasing the size of the cluster.

As a consequence of the aforementioned findings, we propose that the low energy isotopic scrambling in the above reaction proceeds through the following steps:

- a) formation of the collisional complex $[\text{H}^+(\text{H}_2\text{O})_n\text{D}_2\text{O}]^*$ in a vibro-rotational excited state;
- b) incorporation of the heavy water molecule in the cluster "core" as HD_2O^+ by means of isomerization processes involving molecular shifts;
- c) displacement of a solvation molecules from the first shell of HD_2O^+ with the synchronous shift of a D^+ to a neighbor water molecule;
- d) expulsion of one of the isotopic variant of water (H_2O , D_2O or HDO) from the periphery of the complex.

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